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Charge distribution in PVDF/PMMA blends under DC field

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ABSTRACT

The charge distribution in poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA) blends under direct current (DC) electrical field was measured by the pulsed electro-acoustic method (PEA). It was found that the field distribution tended to be uniform and the amount of charges were much smaller than the values estimated by the ordinary additive rule in the PVDF/PMMA blends. Differential scanning calorimeter (DSC), wide-angle X-ray diffraction (WAXD), dynamic mechanical thermal analysis (DMA) and scanning electron microscopy (SEM) were employed to investigate the miscibility and phase structures of PVDF/PMMA blends. The results show that the amorphous regions in the blends comprised amorphous PVDF regions and the miscible PVDF/PMMA regions. At low concentrations of PMMA, the miscible domains were separated and could not transport charges effectively. When the PMMA concentration increased, more and more miscible domains became a continuous phase, and charges could be transported easily and effectively through the miscible phase because polar groups of PMMA could act as hopping sites for charge transportation. Therefore, the decrease in charge amount could be attributed to changes of phase structure and excellent miscibility of the blends.

1. Introduction

Fluorocarbon polymers are widely used as an insulation material in special cables, because of their outstanding electrical and mechanical properties. However, fluorocarbon polymers tend to store charges and become electrets under certain conditions. In the case of direct current (DC) voltage application, the accumulation of charges can distort the electric field distribution in the polymer insulation matrix. When the distorted electric field is strong enough, the electrical tree initiation and breakdown will occur in the material [1,2], which usually leads to apparatus failure. Therefore it is important to understand the mechanism of the formation and accumulation of charges in fluorocarbon polymers and to explore the means of improvement.

The space charge distribution can be improved by various methods such as blending with polar materials, surface modifications and importing polar groups in polymer chains. Many researches were performed to investigate the space charge distribution in polyolefins [3–6]. As far as charge distribution in PVDF is concerned, most researches were focused on the pyroelectric and piezoelectric behavior of PVDF electrets [7–9]. However, the damages of charges were ignored when PVDF was used as an insulation material for low frequency cables [10]. There were few researches on how to diminish the amount of charges and improve the charge distribution in PVDF. The aim of this paper is to present a simple and effective way to reduce the amount of charges in PVDF.

The miscibility of PVDF/PMMA blends has been studied extensively since the 1970s. The blends have been found to be completely miscible over the entire composition range above the PVDF melting temperature (T_m) of 170 °C and below lower critical solution temperature (LCST) of 330 °C. According to most studies [11,12], PVDF can crystallize in the blends if its weight fraction exceeds 0.5 while form a completely amorphous phase if its weight fraction is under 0.5. The miscibility of these two polymers has been evaluated by means such as the transparency of the blends, the Flory–Huggins interaction parameter, the glass transition temperature and so on. One of the commonly used methods is the determination of T_m depressions of PVDF crystals by Nishi and Wang [13]. It is concluded that the miscibility between PVDF and PMMA is stereoselective. Some researchers [13,14] believe that the miscibility of PVDF/(iso-PMMA) is better than that of PVDF/(syn-PMMA). However, others [15] show that both PVDF/at-PMMA and PVDF/syn-PMMA systems are more miscible than PVDF/iso-PMMA. Nevertheless, it is confirmed that PVDF/PMMA is completely miscible regardless of configurations.

Here charge distribution of PVDF is improved by blending with PMMA. The relationship between the charge transportation and the phase structure of the blends is discussed.

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Table 1
Parameters derived from DSC.

No.	PMMA/PVDF (by wt)	T_m (°C)	ΔH_m (J g^{-1})	T_c (°C)	ΔH_c (J g^{-1})
PVDF	0.00/1.00	166.6	34	139.6	41
PVDF95	0.05/0.95	165.4	30	140.7	39
PVDF90	0.10/0.90	165.1	32	138.4	38
PVDF85	0.15/0.85	164.1	30	138.4	35
PVDF80	0.20/0.80	163.4	27	137.0	34
PVDF72	0.28/0.72	163.2	25	131.1	30
PVDF60	0.40/0.60	160.3	21	125.4	24
PVDF50	0.50/0.50	155.0	11		

2. Experimental

2.1. Materials and preparation of specimens

PVDF was the product of 3F New Materials Co. Ltd., Shanghai, China by the trade name of FR902, and PMMA was the product of Chimei Co., Taiwan, China by the trade name of CM205 (iso-PMMA:at-PMMA:syn-PMMA = 17:90:3). PVDF and PMMA were dried at 90 °C for 24 h in a vacuum oven. Then PMMA and PVDF were mixed in a mixer of Brabender Plasticorder with rotor speed of 40 rev min^{-1} at 205 °C for 5 min. As references, the virgin PVDF and PMMA were subjected to the same process used for the blends. All the blends were hot pressed to films with thickness of 0.30 mm at 195 °C. The compositions of the samples were listed in Table 1.

2.2. Differential scanning calorimeter (DSC) analysis

A PerkinElmer DSC-7 differential scanning calorimeter was used for non-isothermal investigations. The instrument was calibrated by zinc and indium. The weight of specimen was about 12 mg and all experiments were carried out under nitrogen protection. The specimens were first heated up to 220 °C (50 °C higher than the melting point of PVDF) at rate of 10 °C min^{-1} and held for 3 min at this temperature in order to erase previous morphological history. Then the specimens were cooled to 50 °C at cooling rate of 10 °C min^{-1} and heated up to 220 °C again at rate of 10 °C min^{-1}.

2.3. Wide-angle X-ray diffraction (WAXD) test

A D/max-rB diffractometer (Rigaku, Japan) equipped with a Cu Kα tube and Ni filter was employed to investigate the crystalline form of the specimens over a range of diffraction angle 2θ of 5–50°.

2.4. Dynamic mechanical thermal analysis (DMA)

A DMA242 instrument (Netzsch, Germany) was employed. The tensile mode was used and the parameters were selected as follows: temperature range (−100 to 110 °C), frequency (1 Hz), heating rate (3 °C min^{-1}), amplitude (20 μm), driving force (3 N).

2.5. Scanning electron microscope (SEM) observation

A scanning electron microscope (TESCAN 5136MM) was employed to investigate the phase structures of blends. The samples were fractured in liquid nitrogen and then immersed in chloroform at 10 °C for 24 h to etch the PMMA rich phase. The cross section of the sample was coated with gold–palladium and observed.

2.6. Space charge measurement

The space charge distribution in samples was measured using the pulsed electro-acoustic (PEA) method as shown in Fig. 1 (DC source, 0–40 kV; pulse width, 20 ns; pulse voltage, 0–1 kV). The diameter of the copper electrode was 25 mm. Aluminum was deposited on two sides of plate samples as an electrode. Silicone oil was used as an acoustic coupling agent in order to make a good acoustic contact between the sample electrode and the measuring electrode.

3. Results and discussion

3.1. Space charge distribution in PMMA/PVDF blends

Fig. 2 shows the charge distributions in the blends, measured with the field still applied, after DC stresses of 10, 20, 30, and 40 kV mm^{-1} have been applied for 30 min. It can be seen that the charge density increases with the voltage, but to different extents for the blends of various compositions. The charges in all samples are mainly heterocharges under DC voltages because the prominent negative charges are observed near the anode in the bulk, though some homocharges appear at the surface of the samples because of induction [4,5,16–18]. In general, the heterocharges in polymer insulator originates from dipole orientation and polarization and dissociation of chain ends and low-molecular-mass species such as impurities, initiator residues and additives generated in the course of synthesis and processing [18]. The positive charges are not observed evidently near the cathode, which could probably be attributed to the neutralization of the heterocharges by the electrons injected from the cathode. However, the injection of positive charges from the anode is difficult due to the lower mobility of holes than electrons. Therefore, the obvious negative charges near the anode can be observed.

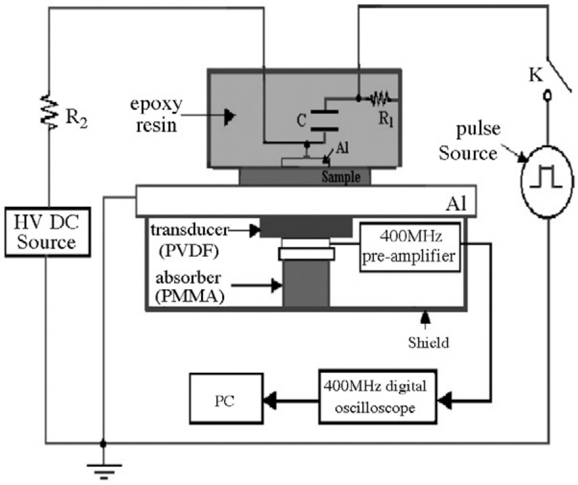

Fig. 1. Schematic diagram of PEA apparatus for measurement of charge distribution.

Fig. 3 shows the charge distributions after the applied fields are removed and the specimen is short-circuited immediately. Most charges disappear at electrodes or are neutralized by heterocharges, while a few charges are trapped and remain in the bulk. Except the heterocharges remaining in the bulk, no homocharges are found in Fig. 3. Furthermore, very small residual charges at higher PMMA concentration indicate that the polar groups of PMMA can act as hopping sites for charge transportation.

Fig. 4 shows the relative charge amount versus the concentration of PMMA in the blends by weight percentage. The amount of space charges is calculated from the integral of the peak area of the PEA diagram. It can be found that the higher PMMA concentration, the less charges in the samples. The experimental values of the blends are compared with those expected by additive rule of pure PVDF and PMMA. The charge amount shows a negative deviation from the simply additive rule. It is interesting to note that the charge amount decrease rapidly at the low PMMA concentrations (below 28 wt%). In contrast, the charge amount decreases unconspicuously at high PMMA concentrations. This may have a close relationship with the phase structures of the blends and the miscibility of two polymers.

3.2. Crystalline behavior and miscibility of PVDF/PMMA blends

Fig. 5 shows the DSC thermograms of melting at second run and crystalline behaviors for PVDF/PMMA blends at the rate of 10 °C min^{-1}, and Table 1 lists the thermodynamic and crystalline parameters derived from Fig. 5. It is obvious that the melting point T_m and the crystalline temperature T_c decrease while the half-peak widths increase when the PMMA concentrations increase.